Supporting Information

In situ generation of less accessible Boc-imines from aldehydes: Construction of a quaternary carbon by Mannich reaction or unprecedented aldol reaction

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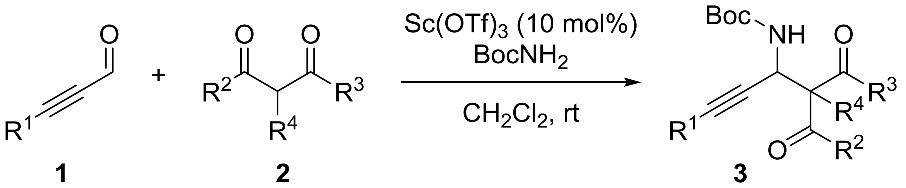
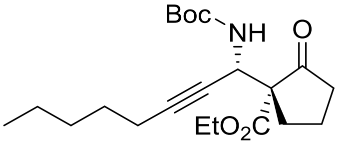
General Information. ^{1}H NMR spectra were measured on a JEOL JNM-FX400 (400 MHz) spectrometer and a JEOL JNM-ECA500 (500 MHz) spectrometer. Data were reported as follows: chemical shifts in ppm from tetramethylsilane or the residual solvent as an internal standard, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin. = quintet, dd = double-doublet, td = triple-doublet, qd = quadruple-doublet, m = multiplet, br = broad, and app = apparent), coupling constants (Hz), and assignment. ^{13}C NMR spectra were measured on a JEOL JNM-FX400 (100 MHz) spectrometer and a JEOL JNM-ECA500 (125 MHz) spectrometer with complete proton decoupling. Chemical shifts were reported in ppm from the residual solvent as an internal standard. High-resolution mass spectra (HRMS) were performed on Thermo Scientific Exactive Plus. For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF254, 0.25 mm) were used. The products were purified by flash column chromatography on neutral silica gel 60N (Kanto Chemical Co. Inc., 40-50 μm). Dichloromethane were purchased from Wako Pure Chemical Industries Co. Inc. Simple chemicals were purchased and used as such. ^{1}H-NMR, ^{13}C-NMR and Mass spectral data of **3a**, **5a** and **5b** have been reported in the previous work.[1]

General procedure for the three-component direct Mannich reaction



To a mixture of ynal **1** (0.10 mmol), β-dicarbonyl **2** (0.11 mmol) and $BocNH_2$ (23.4 mg, 0.20 mmol) in dichloromethane (1.0 mL) was added $Sc(OTf)_3$ (4.9 mg, 0.01 mmol) or $Cu(OTf)_2$ (3.6 mg, 0.01 mmol) at room temperature. After stirring for 24-48 h, the mixture was directly purified by silica gel chromatography (AcOEt/hexane (=1/3) as eluent) to afford the diastereo-mixture of Mannich adduct **3**.

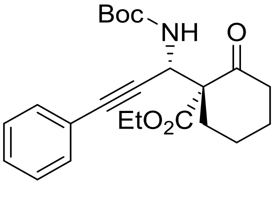
Ethyl 1-(1-((*tert*-butoxycarbonyl)amino)-oct-2-yn-1-yl)-2-oxocyclopentane-carboxylate (3b)



Was obtained as an oil (28.4 mg, 0.075 mmol, 75%, dr = 1.7/1), following the general procedure with 2-octynal (**1b**) (14 μL, 0.1 mmol) and ethyl 2-oxocylopentanecarboxylate (**2a**) (16 μL, 0.1 mmol). The relative configuration of the major diastereomer was determined by ^{1}H NMR spectra of **3b** with the literature data[2] and is shown in the figure above.

^{1}H-NMR (400 MHz, $CDCl_3$): both diastereomers δ 5.96 (d, J = 9.1 Hz, 0.4H, NHBoc), 5.23 (br s, 0.6H, NHBoc), 4.99-4.90 (m, 1H, C*H*NHBoc), 4.25-4.11 (m, 2H, OCH_2CH_3), 2.64-2.19 (m, 4H, CH_2), 2.19-2.09 (m, 2H, CH_2), 2.09-1.86 (m, 2H, CH_2), 1.49-1.44 (m, 1.2H, CH_2), 1.42 (s, 9H, $C(CH_3)_3$), 1.37-1.30 (m, 2.8H, CH_2), 1.29-1.23 (m, 3H, OCH_2CH_3), 0.89 (m, 3H, CH_3)
^{13}C-NMR (125 MHz, $CDCl_3$): both diastereomers δ 215.0, 210.4, 170.1, 168.9, 154.9, 154.8, 85.2, 84.7, 80.0, 79.6, 76.5, 76.2, 64.9, 62.8, 61.70, 61.68, 45.7, 45.3, 39.0, 37.7, 32.9, 31.0, 30.9 (two peaks overlap), 28.3, 28.21 (two peaks overlap), 28.16, 22.1 (two peaks overlap), 19.6, 19.1, 18.5 (two peaks overlap), 13.99, 13.98, 13.92, 13.91
HRMS (ESI): calcd. for $C_{21}H_{33}NNaO_5^+$ $(M+Na)^+$: 402.2251, found: 402.2253

Ethyl 1-(1-((*tert*-butoxycarbonyl)amino)-3-phenylprop-2-yn-1-yl)-2-oxocyclohexanecarboxylate (3c)



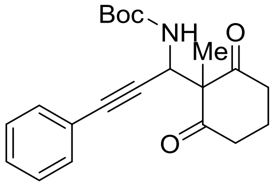
Was obtained as a viscous oil (33.8 mg, 0.085 mmol, 85%, dr = 4.2/1), following the general procedure with 3-phenyl-2-propynal (**1a**) (12 μL, 0.1 mmol) and ethyl 2-oxocylohexanecarboxylate (**2b**) (18 μL, 0.11 mmol). The relative configuration of the major diastereomer was determined by ^{1}H NMR spectra of **3c** with the literature data[2] and is shown in the figure above.

^{1}H-NMR (400 MHz, $CDCl_3$): both diastereomers δ 7.46-7.33 (m, 2H, Ph), 7.33-7.18 (m, 3H, Ph), 5.89 (d, J =9.2 Hz, 0.2H, NHBoc), 5.65 (d, J = 10.2 Hz, 0.8H, NHBoc), 5.29 (d, J = 10.2 Hz, 0.8H, C*H*NHBoc), 4.97 (d, J = 10.9 Hz, 0.2H, C*H*NHBoc), 4.37-4.18 (m, 2H, $OC\mathit{H}_2CH_3$), 2.71-2.36 (m, 3H, CH_2), 2.22-2.06 (m, 1H, CH_2), 1.98-1.79 (m, 2.4H, CH_2), 1.79-1.65 (m, 0.8H, CH_2), 1.65-1.56 (m, 0.8H, CH_2), 1.44 (s, 7.2H, $C(CH_3)_3$), 1.42 (s, 1.8H, $C(CH_3)_3$), 1.29 (t, J = 7.1 Hz, 2.4H, $OCH_2C\mathit{H}_3$), 1.26 (t, J = 7.0 Hz, 0.6H, $OCH_2C\mathit{H}_3$)

^{13}C-NMR (125 MHz, $CDCl_3$): both diastereomers δ 207.1, 206.8, 170.4, 170.3, 155.2, 154.7, 131.73, 131,71, 128.33, 128.26, 128.12, 128.10, 122.6, 122.4, 86.2, 85.5, 84.3, 84.1, 80.2, 79.7, 66.4, 65.1, 61.9, 61.7, 47.7, 45.9, 41.2, 40.3, 34.7, 33.3, 28.3, 28.2, 27.2, 26.1, 22.2, 21.4, 14.04, 13.97

HRMS (ESI): calcd. for $C_{23}H_{29}NNaO_5^+$ $(M+Na)^+$: 422.1938, found: 422.1938

***tert*-Butyl (1-(1-methyl-2,6-dioxocyclohexyl)-3-phenylprop-2-yn-1-yl)carbamate (3d)**



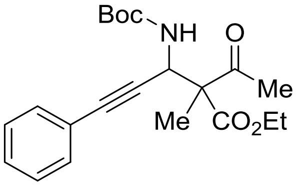
Was obtained as a white solid (22.7 mg, 0.064 mmol, 64%), following the general procedure with 3-phenyl-2-propynal (**1a**) (12 μL, 0.10 mmol) and 2-methyl-1,3-cyclohexanedione (**2c**) (13.9 mg, 0.11 mmol).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.40-7.18 (m, 5H, Ph), 5.53 (d, J = 9.9 Hz, 1H, NHBoc), 5.38 (d, J = 10.2 Hz, 1H, C*H*NHBoc), 2.90-2.61 (m, 2H, CH_2), 2.73 (t, J = 6.8 Hz, 2H, CH_2), 2.09-1.88 (m, 2H, CH_2), 1.45 (s, 9H, $C(CH_3)_3$), 1.37 (s, 3H, CH_3)

^{13}C-NMR (125 MHz, $CDCl_3$): δ 209.6, 207.5, 155.1, 131.7, 128.6, 128.2, 122.1, 86.2, 84.4, 80.3, 68.4, 46.5, 38.8, 38.1, 28.3, 18.1, 17.4

HRMS (ESI): calcd. for $C_{21}H_{25}NNaO_4^+$ $(M+Na)^+$: 378.1676, found: 378.1686

Ethyl 2-acetyl-3-((*tert*-butoxycarbonyl)amino)-2-methyl-5-phenylpent-4-ynoate (3e)



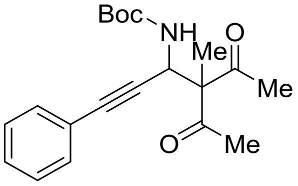
Was obtained as a viscous oil (29.2 mg, 0.078 mmol, 78%, dr = 1.3/1), following the general procedure with 3-phenyl-2-propynal (**1a**) (12 μL, 0.10 mmol) and ethyl 2-methylacetoacetate (**2d**) (16 μL, 0.11 mmol).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.40-7.34 (m, 2H, Ph), 7.34-7.20 (m, 3H, Ph), 5.77 (d, J = 9.6 Hz, 0.6H, NHBoc), 5.48 (d, *J* = 8.8 Hz, 0.4H, NHBoc), 5.31-5.09 (m, 1H, C*H*NHBoc), 4.32-4.19 (m, 2H, OCH_2CH_3), 2.28 (s, 1.3H, $COCH_3$), 2.25 (s, 1.7H, $COCH_3$), 1.60 (s, 1.3H, CCH_3), 1.59 (s, 1.7H, CCH_3), 1.44 (s, 9H, $C(CH_3)_3$), 1.31 (td, *J* = 7.1, 0.9 Hz, 1.7H, OCH_2CH_3), 1.29 (td, *J* = 7.1, 0.9 Hz, 1.3H, OCH_2CH_3)

^{13}C-NMR (125 MHz, $CDCl_3$): δ 204.5, 204.3, 170.9, 170.6, 154.9, 154.8, 131.8 (two peaks overlap), 128.54, 128.45, 128.26, 128.23, 122.4, 122.3, 85.8, 85.4, 84.33, 84.3, 80.3, 80.1, 64.7, 63.6, 61.9, 61.8, 47.7 (two peaks overlap), 28.32, 28.27, 27.6, 26.0, 18.8, 18.2, 14.1, 14.0

HRMS (ESI): calcd. for $C_{21}H_{27}NNaO_5^+$ $(M+Na)^+$: 396.1781, found: 396.1782

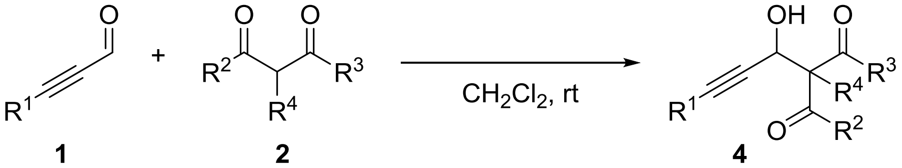
tert-Butyl (4-acetyl-4-methyl-5-oxo-1-phenylhex-1-yn-3-yl)carbamate (3f)



Was obtained as a white solid (28.7 mg, 0.084 mmol, 84%), following the general procedure with 3-phenyl-2-propynal (**1a**) (12 μL, 0.10 mmol) and 3-methyl-2,4-pentanedione (**2e**) (18 μL, 0.11 mmol).

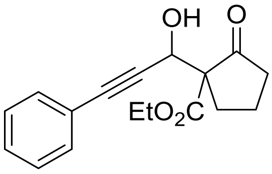
^{1}H-NMR (500 MHz, CDCl$_3$): δ 7.38-7.36 (m, 2H, Ph), 7.31-7.27 (m, 3H, Ph), 5.54 (br s, 1H, NHBoc), 5.26 (d, J = 10.2 Hz, 1H, CHNHBoc), 2.24 (s, 3H, COCH$_3$), 2.22 (s, 3H, COCH$_3$), 1.64 (s, 1H, CH$_3$), 1.44 (s, 1H, C(CH$_3$)$_3$)
^{13}C-NMR (125 MHz, CDCl$_3$): δ 206.3, 206.2, 155.0, 131.7, 128.5, 128.2, 122.2, 85.4, 84.5, 80.4, 69.1, 47.3, 28.2, 27.7, 26.4, 17.9
HRMS (ESI): calcd. for $C_{20}H_{25}NNaO_4^+$ $(M+Na)^+$: 366.1676, found: 366.1680

General procedure for the catalyst-free aldol reaction



A mixture of ynal **1** (0.5 mmol) and β-dicarbonyl **2** (0.5 mmol) was stirred at room temperature. After stirring for 4.5-36 h, the mixture was directly purified by silica gel chromatography (AcOEt/hexane (=1/7) as eluent) with dry ice jacket to afford the diastereo-mixture of aldol adduct **4**.

Ethyl 1-(1-hydroxy-3-phenylprop-2-yn-1-yl)-2-oxocyclopentane-1-carboxylate (4a)

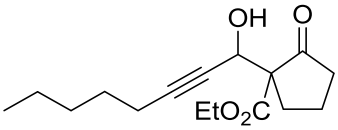


Was obtained after 4.5 h of stirring as a viscous oil (143 mg, 0.50 mmol, 99%, dr = 1.5/1), following the general procedure with 3-phenyl-2-propynal (**1a**) (62 μL, 0.5 mmol) and ethyl 2-oxocylopentanecarboxylate (**2a**) (73 μL, 0.5 mmol).

^{1}H-NMR (500 MHz, CDCl$_3$): both diastereomers δ 7.41-7.39 (m, 2H, Ph), 7.35-7.26 (m, 3H, Ph), 5.27 (d, J = 4.3 Hz, 0.6H, CHOH), 5.16 (d, J = 8.5 Hz, 0.4H, CHOH), 4.27-4.19 (m, 2H, OCH_2CH$_3$), 3.35 (d, J = 8.5 Hz, 0.4H, OH), 3.27 (d, J = 4.5 Hz, 0.6H, OH), 2.67-2.28 (m, 4H, CH$_2$), 2.20-1.98 (m, 2H, CH$_2$), 1.29 (t, J = 7.1 Hz, 1.8H,

OCH_2CH_3), 1.29 (t, *J* = 7.1 Hz, 1.2H, OCH_2CH_3)
^{13}C-NMR (125 MHz, $CDCl_3$): both diastereomers δ 214.8, 212.2, 170.8, 169.2, 131.7, 131.7, 128.8, 128.7, 128.3 (two peaks overlap), 122.0, 121.8, 86.8, 85.7, 65.2, 65.0, 64.9, 64.5, 62.1, 61.9, 39.1, 38.7, 30.5, 29.3, 27.3, 20.9, 20.1, 19.7, 14.0, 13.9
HRMS (ESI): calcd. for $C_{17}H_{18}NaO_4^+$ $(M+Na)^+$: 309.1097, found: 309.1100

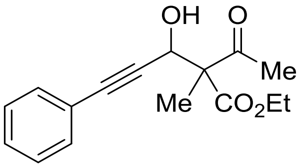
Ethyl 1-(1-hydroxyoct-2-yn-1-yl)-2-oxocyclopentane-1-carboxylate (4b)



Was obtained after 36 h of stirring as an oil (96.3 mg, 0.34 mmol, 68%, dr = 1.4/1), following the general procedure with 2-octynal (**1b**) (71 μL, 0.5 mmol) and ethyl 2-oxocylopentanecarboxylate (**2a**) (73 μL, 0.5 mmol).

^{1}H-NMR (400 MHz, $CDCl_3$): both diastereomers δ 5.03 (m, 0.4H, C*H*OH), 4.91 (m, 0.6H, C*H*OH), 1.24-4.17 (m, 2H, OCH_2CH_3), 3.15 (d, *J* = 8.5 Hz, 0.6H, OH), 3.10 (d, *J* = 4.4 Hz, OH), 2.54-2.41 (m, 2H, CH_2), 2.36-2.20 (m, 2H, CH_2), 1.98 (m, 4H, CH_2), 1.50-1.46 (m, 2H, CH_2), 1.39-1.25 (m, 7H, CH_2, OCH_2CH_3), 0.89 (t, *J* = 6.4 Hz, 1.3H, CH_3), 0.88 (t, *J* = 6.4 Hz, 1.7H, CH_3)
^{13}C-NMR (125 MHz, $CDCl_3$): both diastereomers δ 215.0, 212.4, 171.1, 169.4, 88.0, 87.5, 77.7 (two peaks overlap), 65.1, 64.7, 61.7, 61.3, 54.7 (two peaks overlap), 39.1, 38.0, 30.9, 30.5, 29.1, 28.1, 28.0, 27.3, 22.1, 21.0, 20.0, 19.7, 18.55, 18.52, 14.1, 14.0, 13.93, 13.88
HRMS (ESI): calcd. for $C_{16}H_{24}NaO_4^+$ $(M+Na)^+$: 303.1567, found: 303.1565

Ethyl 2-acetyl-3-hydroxy-2-methyl-5-phenylpent-4-ynoate (4c)

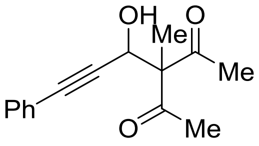


Was obtained after 48 h of stirring in CH_2Cl_2 (0.5 mL) as an oil (56.5 mg, 0.21 mmol, 59%, dr = 1.3/1), following the general procedure with 3-phenyl-2-propynal (**1a**) (12 μL, 0.1 mmol) and ethyl 2-methylacetoacetate (**2d**) (72 μL, 1.0 mmol).

^{1}H-NMR (400 MHz, $CDCl_3$): both diastereomers *δ* 7.42-7.39 (m, 2H, Ph), 7.32-7.25 (m, 3H, Ph), 5.21 (d, *J* = 5.6 Hz, 0.5H, C*H*OH), 5.03 (d, *J* = 8.5 Hz, 0.5H, C*H*OH), 4.33-4.18 (m, 2H, OCH_2CH_3), 3.68 (d, *J* = 8.7 Hz, 0.5H, OH), 3.46 (d, *J* = 5.8 Hz, 0.5H, OH), 2.29 (s, 0.5H, $COCH_3$), 2.27 (s, 0.5H, $COCH_3$), 1.61 (s, 1.5H, CCH_3), 1.57 (s, 1.5H, CCH_3), 1.32 (t, *J* = 7.1 Hz, 1.3H, OCH_2CH_3), 1.28 (t, *J* = 7.1 Hz, 1.7H, OCH_2CH_3)
^{13}C-NMR (100 MHz, $CDCl_3$): both diastereomers *δ* 206.1, 204.1, 171.9, 170.3, 131.76, 131.73, 128.7, 128.6, 128.26, 128.23, 122.1, 122.0, 86.7, 86.6, 85.8, 85.6, 66.5, 66.0, 65.2, 64.4, 62.0, 61.9, 27.3, 26.8, 16.8, 15.6, 14.03, 13.97

HRMS (ESI): calcd. for $C_{16}H_{18}NaO_4^+$ $(M+Na)^+$: 297.1097, found: 297.1100

3-(1-Hydroxy-3-phenylprop-2-yn-1-yl)-3-methylpentane-2,4-dione (4d)



Was obtained after 5 h of stirring as an oil (91 mg, 0.37 mmol, 74%), following the general procedure with 3-phenyl-2-propynal (**1a**) (62 μL, 0.50 mmol) and 3-methyl-2,4-pentanedione (**2e**) (59 μL, 0.50 mmol).

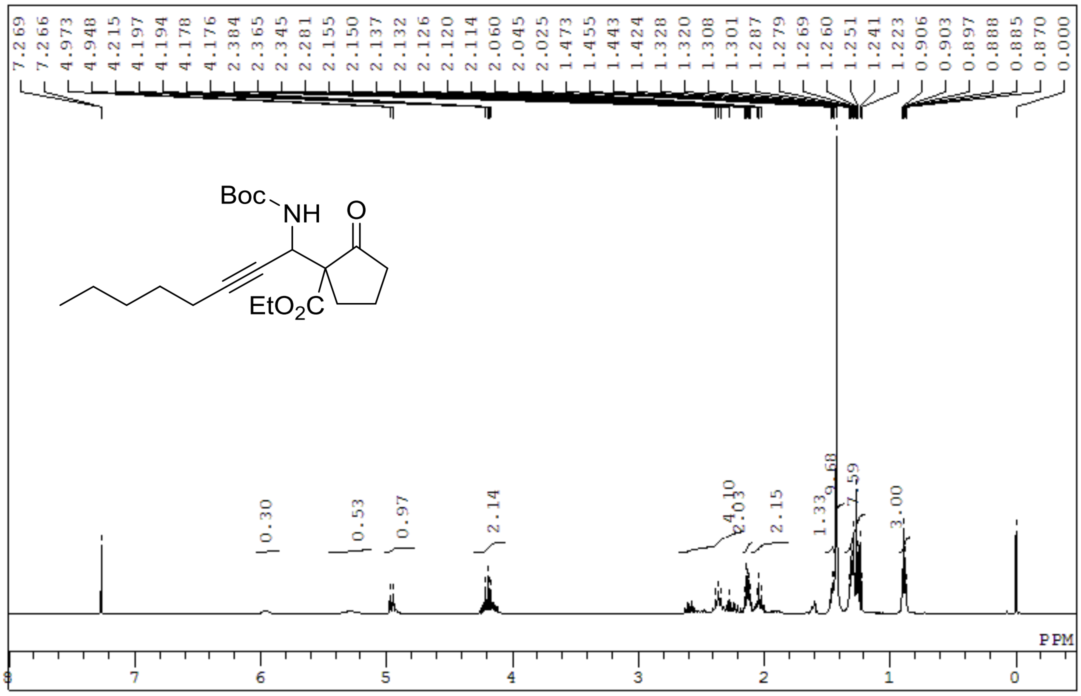
^{1}H-NMR (500 MHz, $CDCl_3$): both diastereomers *δ* 7.43-7.40 (m, 2H, Ph), 7.35-7.28 (m, 3H, Ph), 5.24 (d, *J* = 6.2 Hz, 1H, C*H*OH) 3.27 (d, *J* = 6.0 Hz, 1H, OH), 2.260 (s, 3H, $COCH_3$), 2.257 (s, 3H, $COCH_3$), 1.62 (s, 3H, CCH_3)
^{13}C-NMR (125 MHz, $CDCl_3$): *δ* 207.3, 205.7, 131.7, 128.8, 128.3, 121.8, 87.1, 85.7, 70.7, 65.8, 28.0, 27.2, 15.5

HRMS (ESI): calcd. for $C_{15}H_{16}NaO_3^+$ $(M+Na)^+$: 267.0992, found: 267.0995

Reference

1 T. Kano, T. Yurino, D. Asakawa, K. Maruoka, *Angew. Chem. Int. Ed.* **2013**, *52*, 5532.

2 T. Kano, T. Yurino, K. Maruoka, *Angew. Chem. Int. Ed.* **2013**, *52*, 11509.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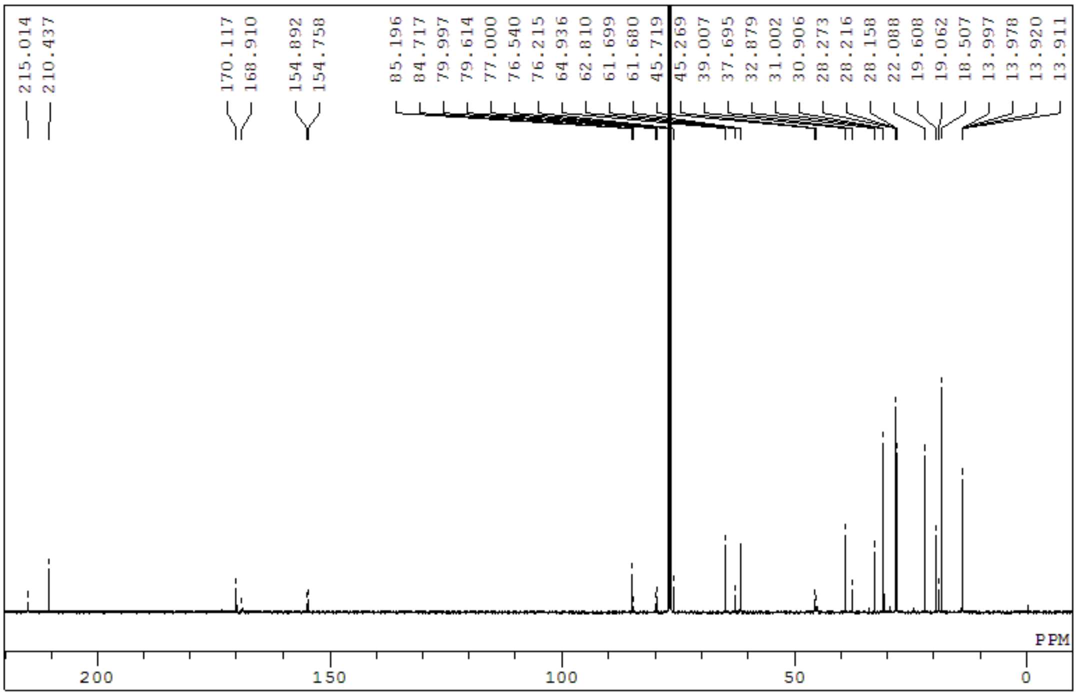
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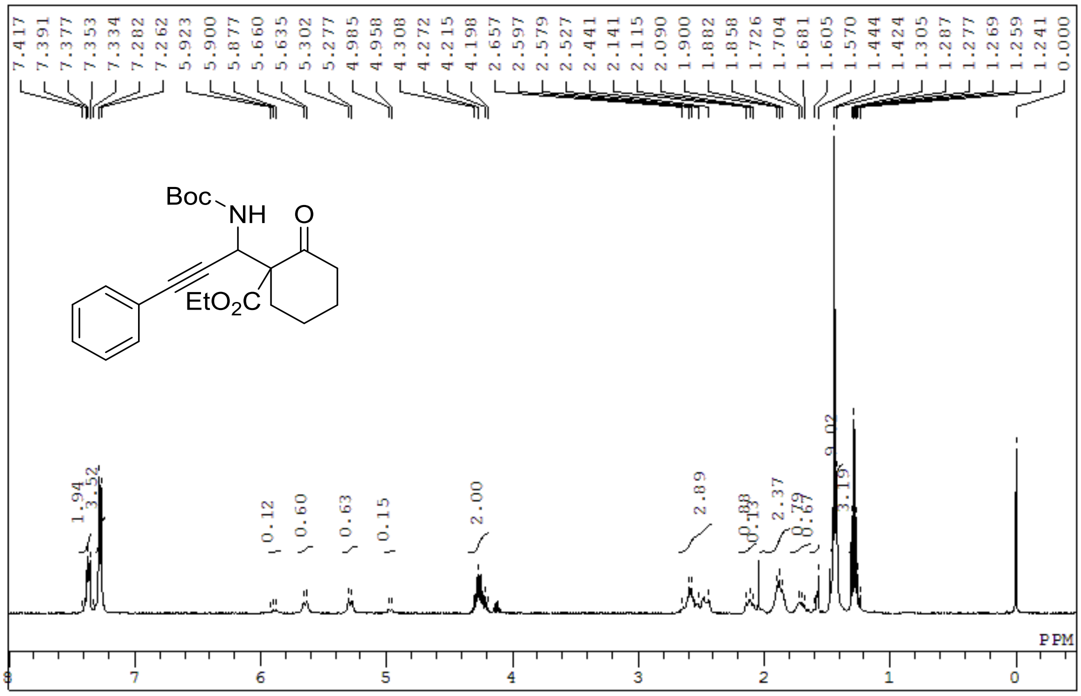
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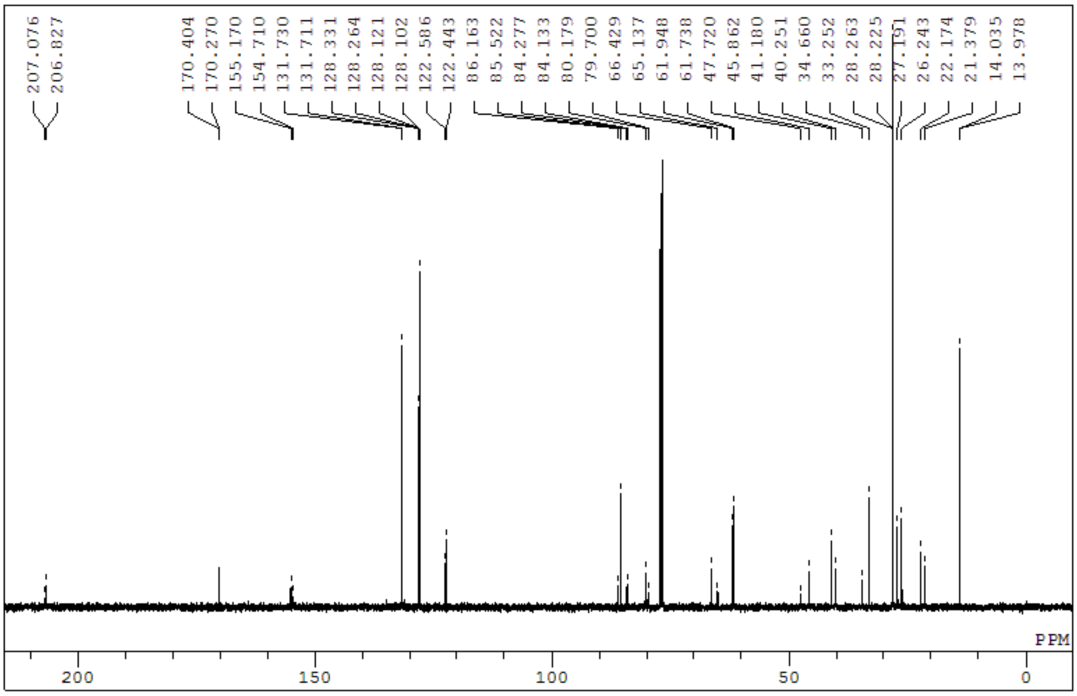
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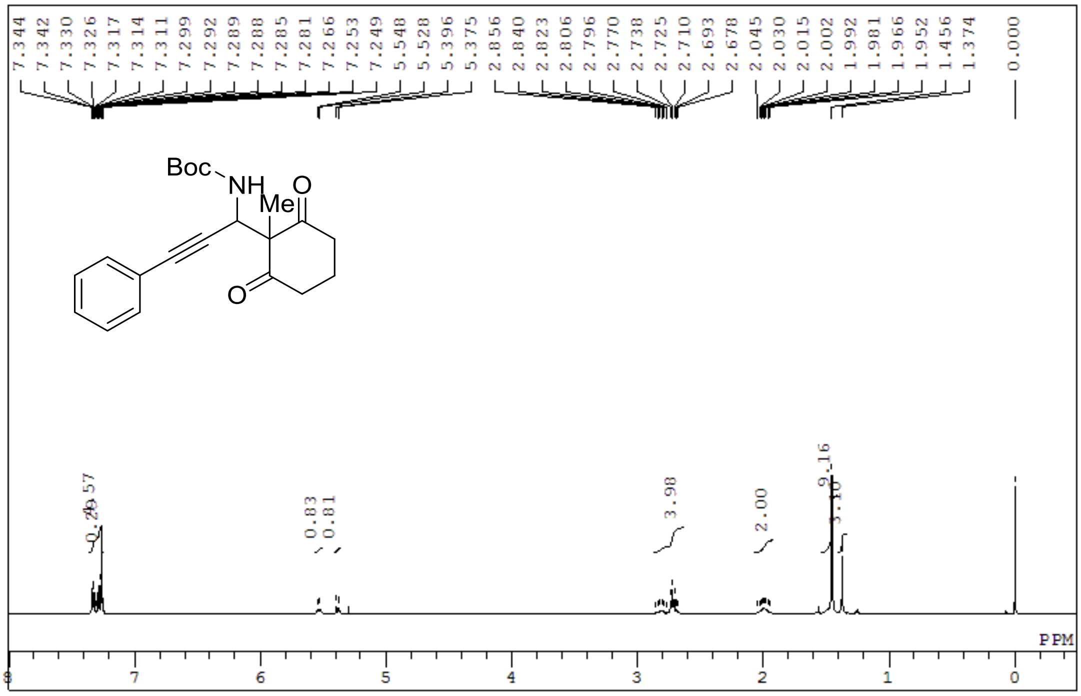
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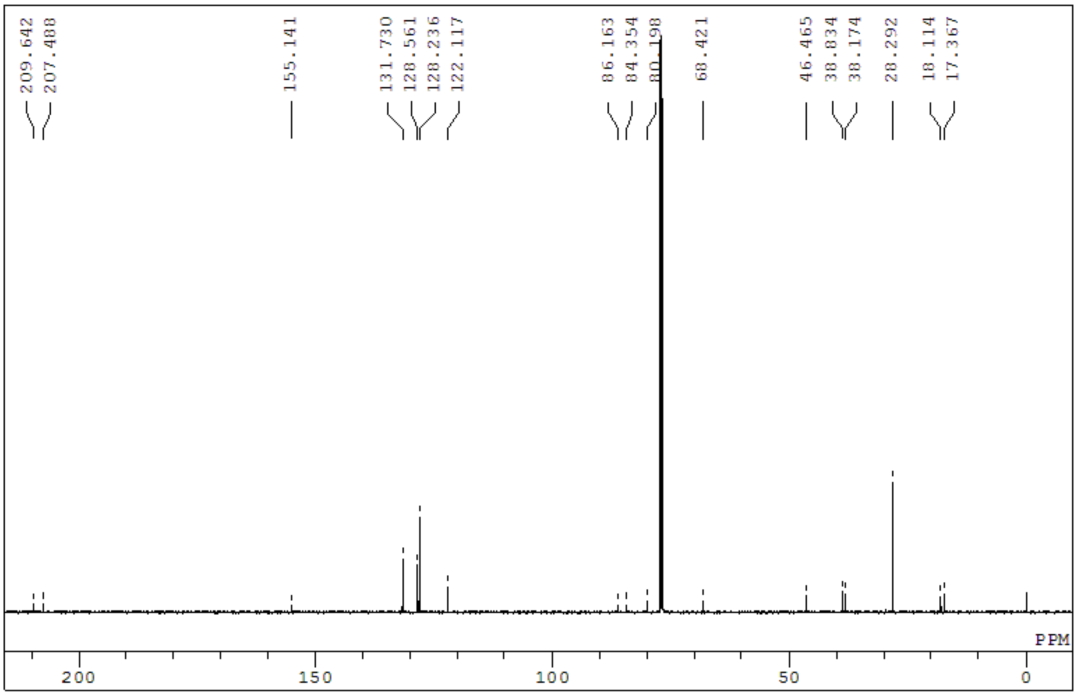
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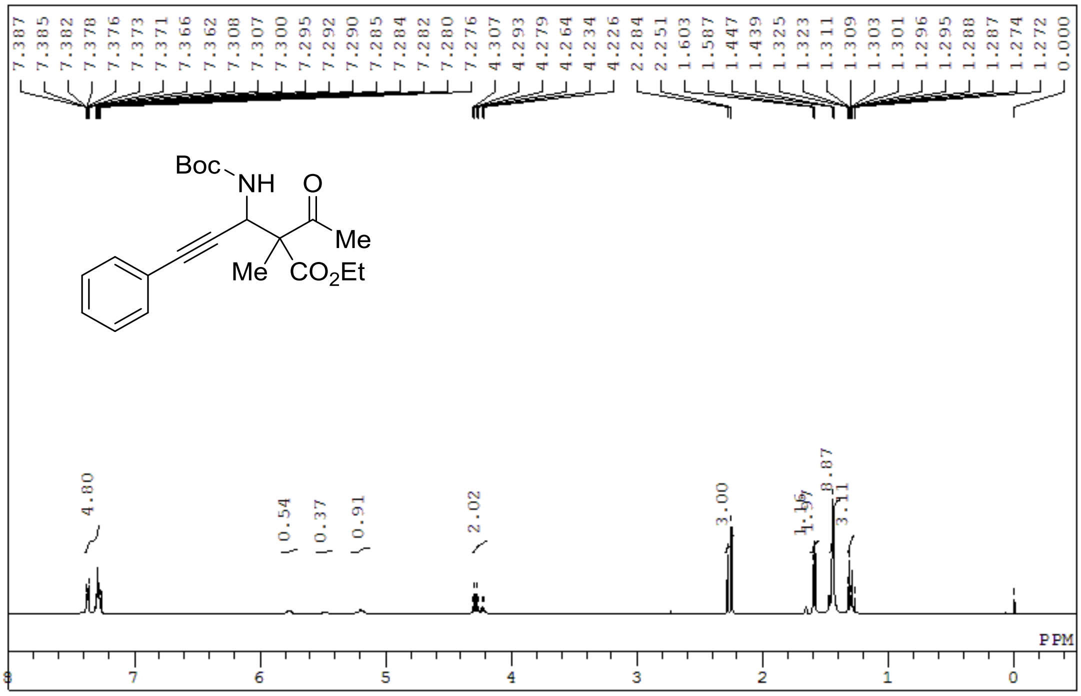
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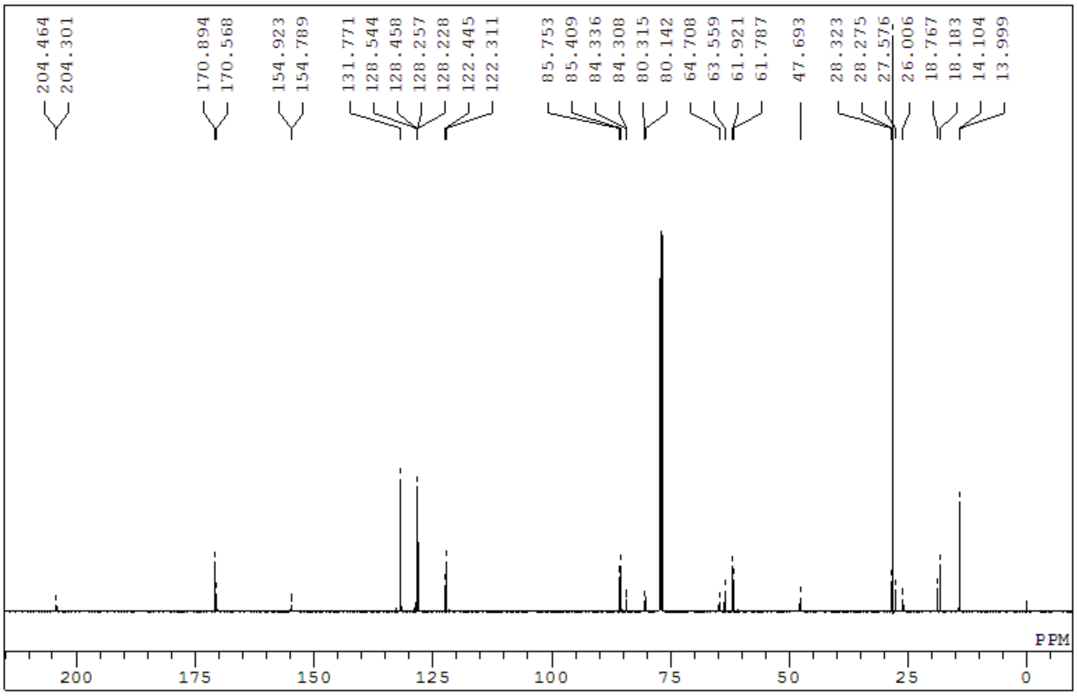
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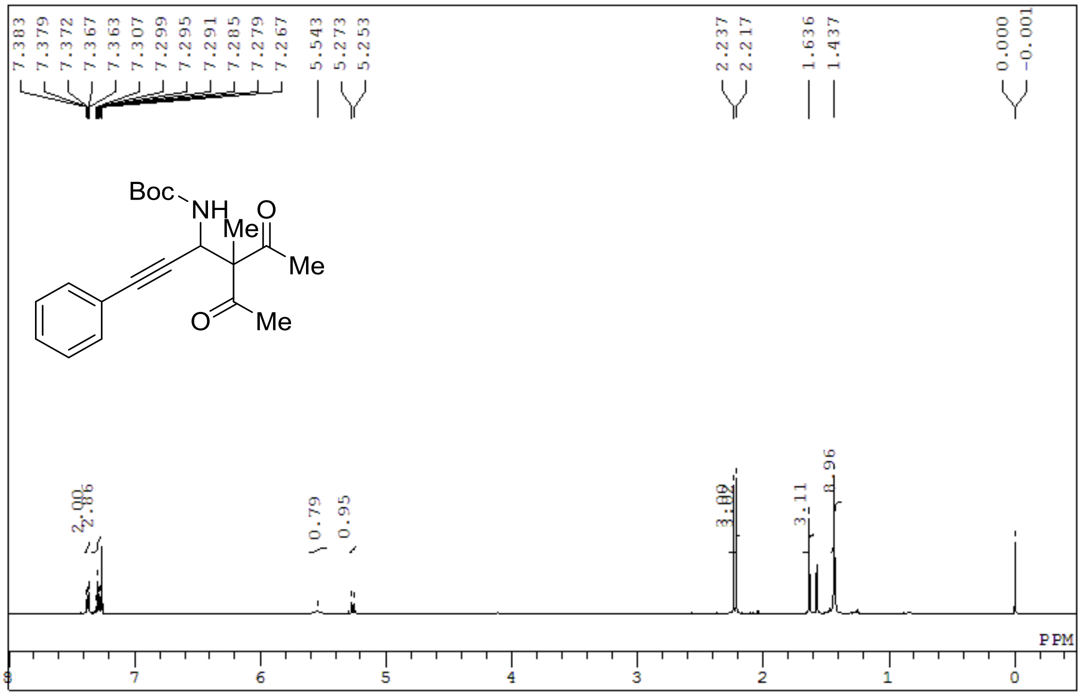
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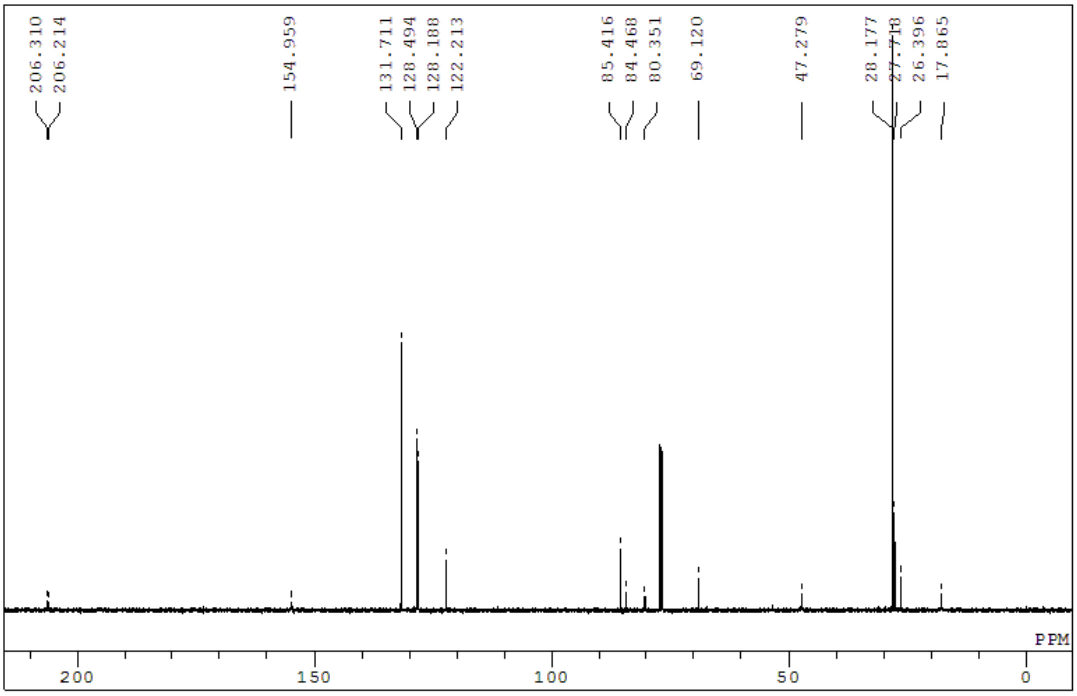
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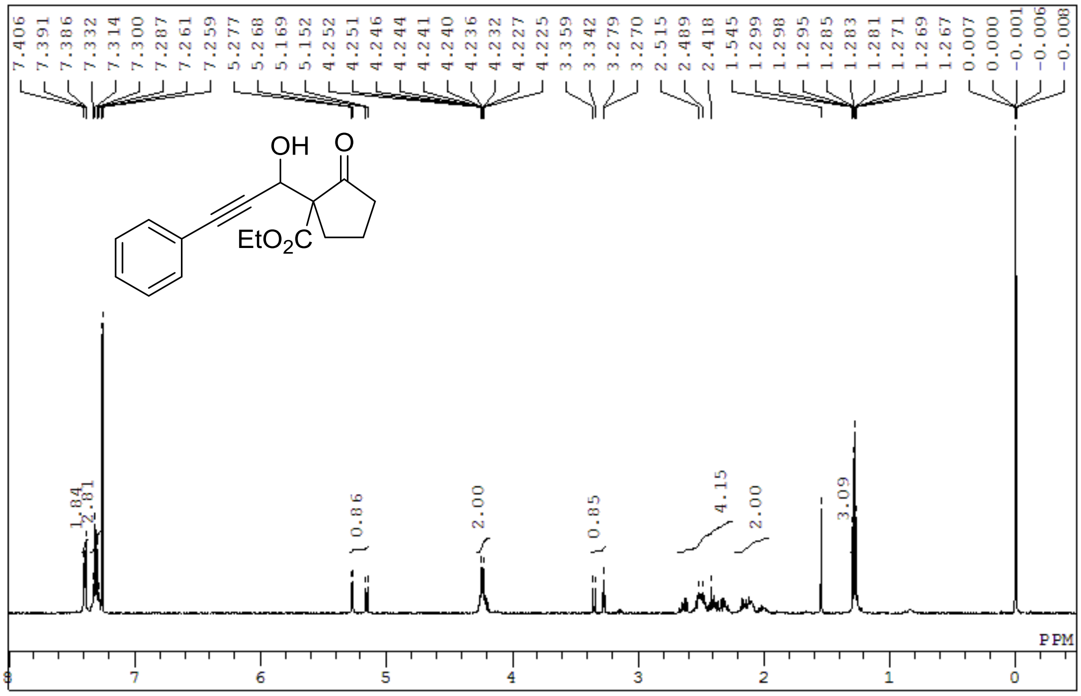
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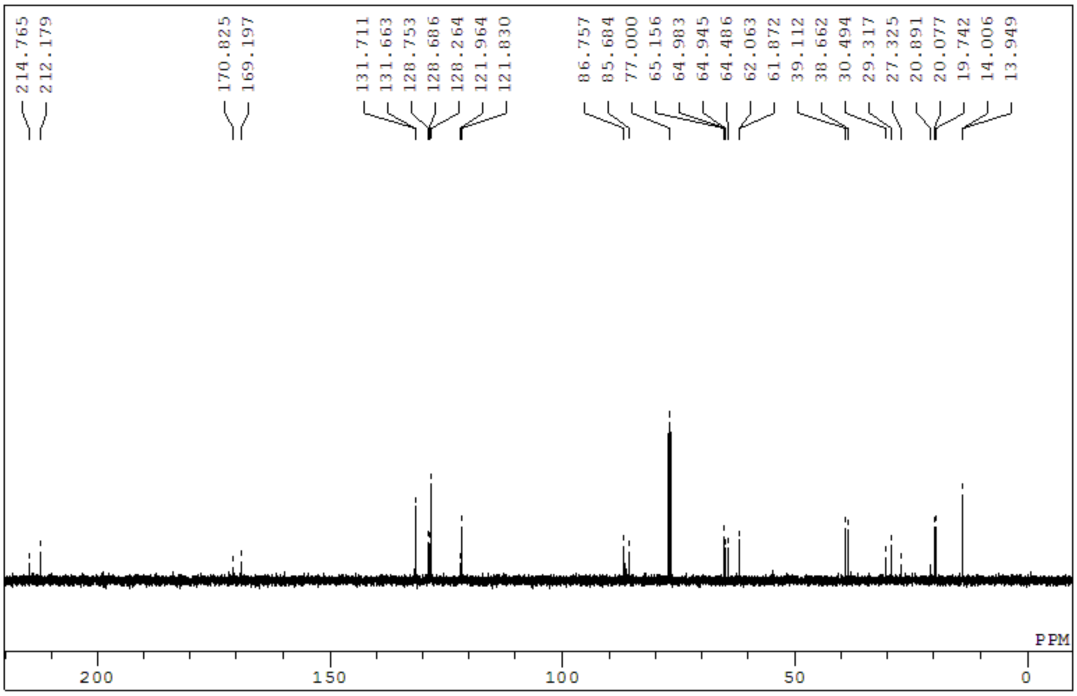
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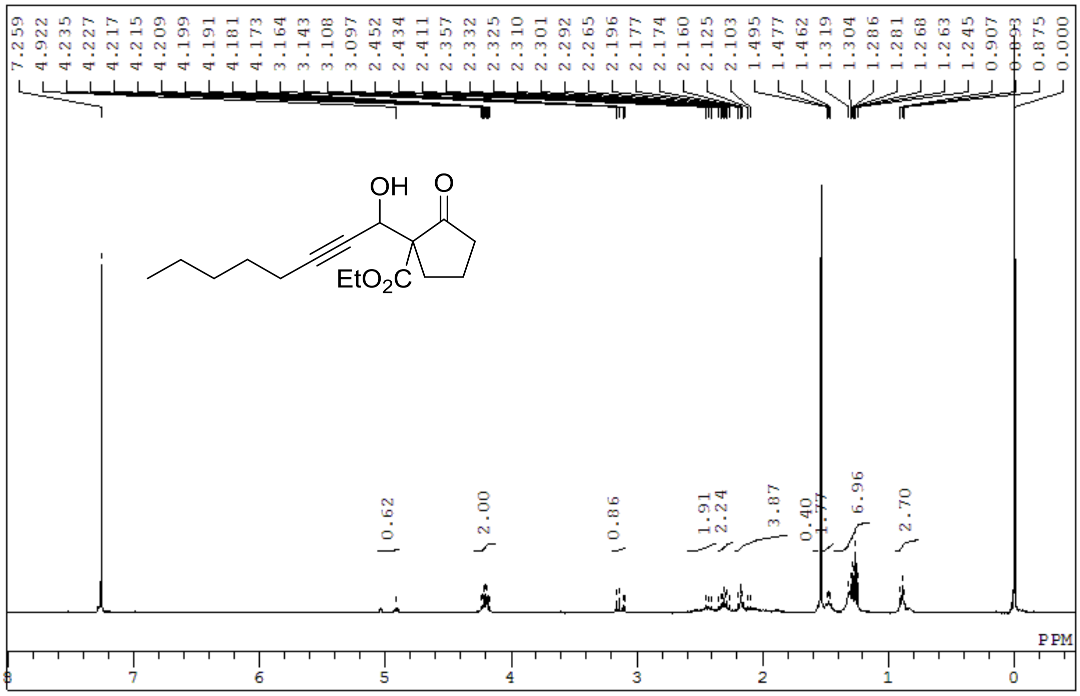
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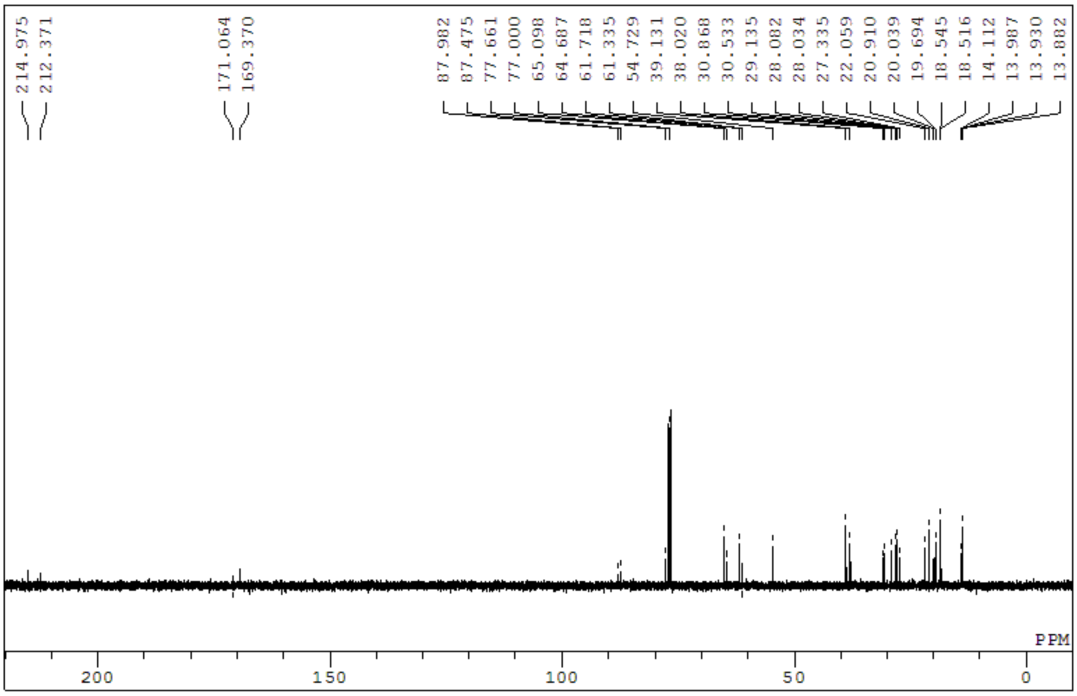
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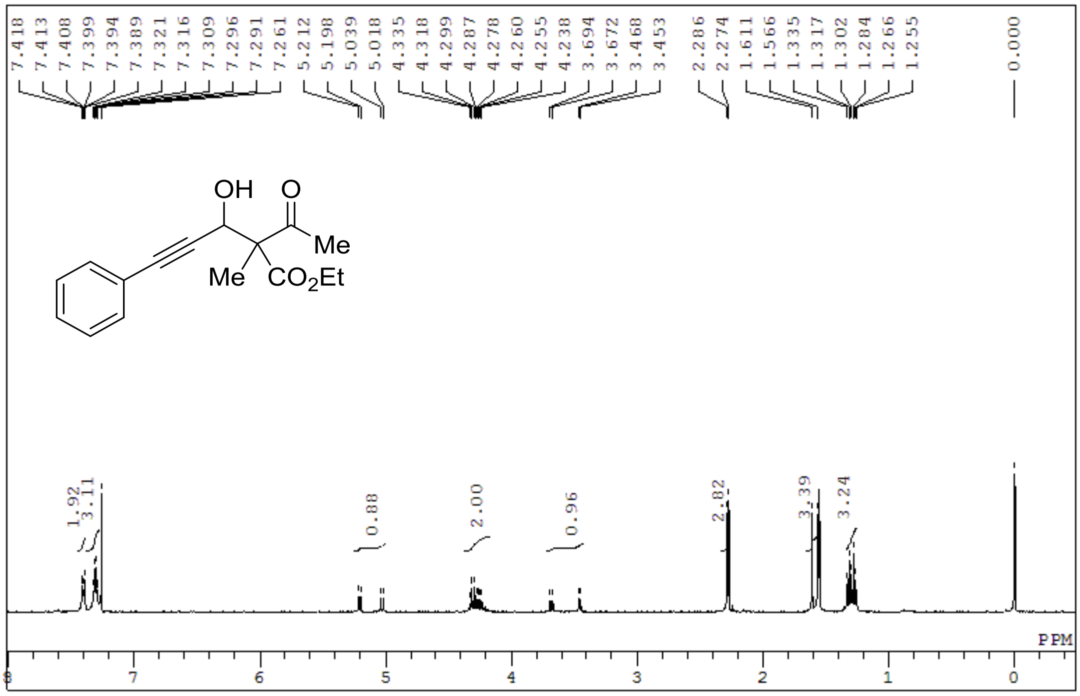
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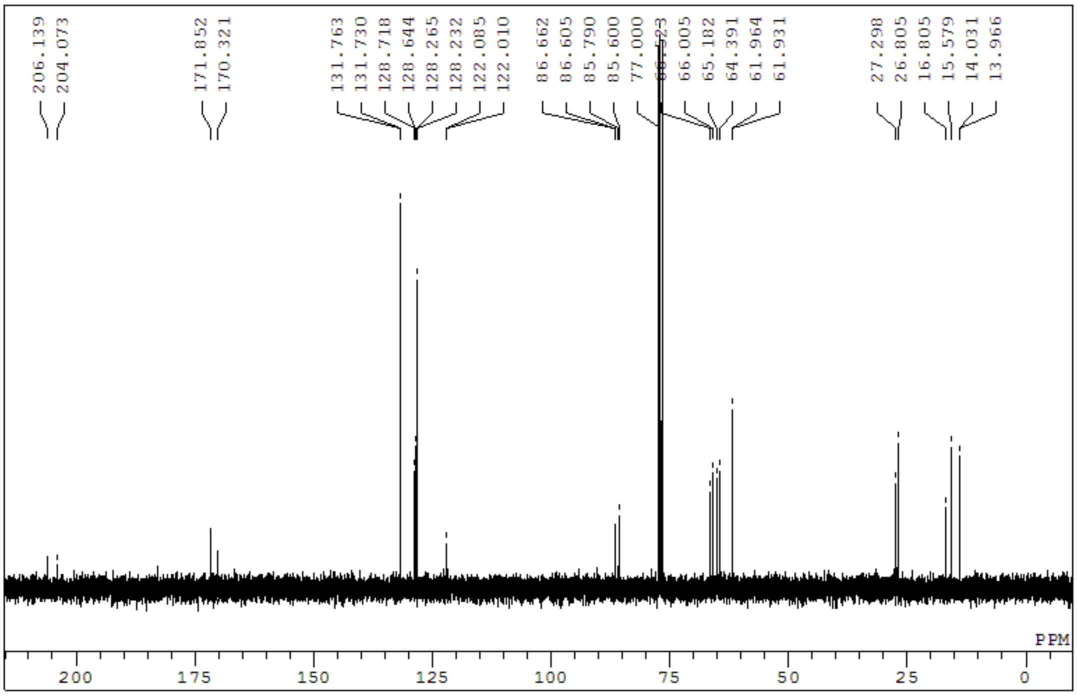
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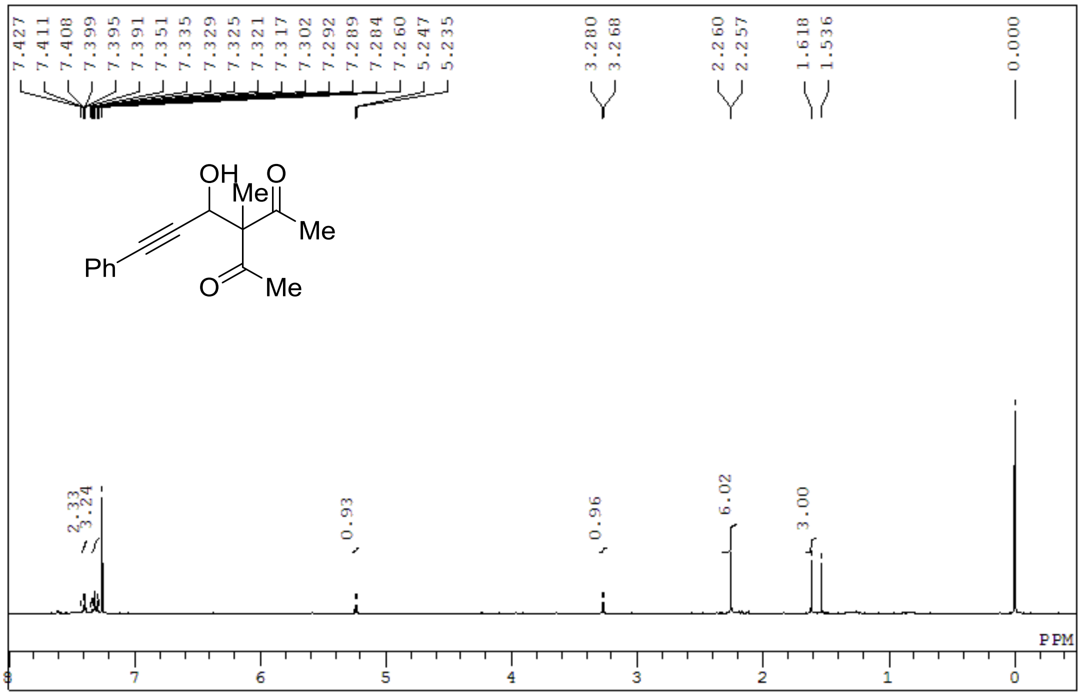
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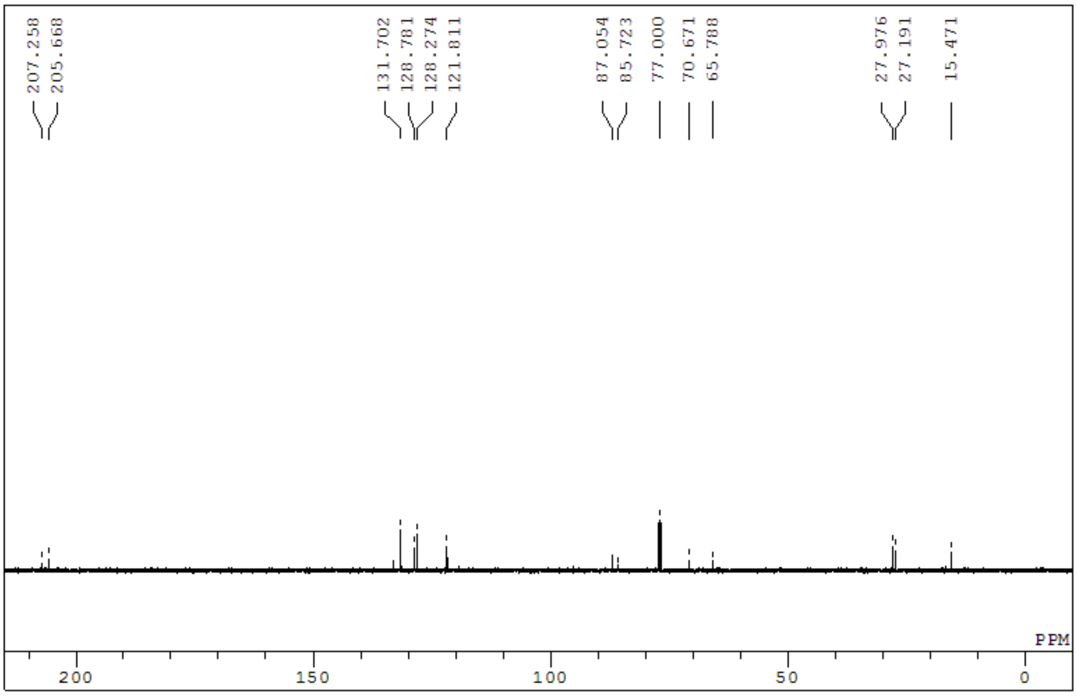
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